

# RAW MATERIALS

UDC 661.882.27.666.65:549.057

## THERMOCHEMICAL TRANSFORMATIONS OF ILMENITE – LEUCOXENE CONCENTRATE

V. É. Grass,<sup>1,2</sup> N. A. Sekushin,<sup>1</sup> and B. A. Goldin<sup>1</sup>Translated from *Steklo i Keramika*, No. 2, pp. 25 – 28, February, 2010.

Porous silicate-ferropseudobrookite composite material manifesting the properties of a ceramic *n*-type semiconductor has been synthesized by vacuum-heat treatment of ilmenite – leucoxene concentrate modified by additions of magnesium oxide. The microstructure and the chemical and phase compositions are described, and the mechanical and electrophysical characteristics of the material obtained are investigated.

**Key words:** ilmenite – leucoxene concentrate, ferrotitanate, ferropseudobrookite, vacuum-heat treatment.

The commercial application of technologies for high-temperature treatment of ilmenite – leucoxene concentrates is limited at the present time mainly by the production of titanium slags, which in turn are used in the production of sponge titanium and pigment titanium dioxide. It is evident that the use of titanium raw material is by no means exhausted by this and scientific – innovative research in this field is topical. Specifically, we have studied the possibility of using ilmenite – leucoxene concentrate as an initial raw material for obtaining functional ferrotitanate materials.

For more than 100 years iron titanates belonging to the pseudobrookite series with the general formula  $\text{Fe}_{1+x}\text{Ti}_{2-x}\text{O}_5$  ( $0 \leq x \leq 1$ ) have been a subject of persistent interest of specialists in such fields as the science of mineralogy, solid-state chemistry and physics, metallurgy, and materials science. Active investigations by means of x-ray and neutron diffraction, EPR, and Mössbauer spectroscopy have established their structural characteristics and made it possible to study their properties and determine the possibility for practical applications. Thus, the prospects for using such compounds in the production of materials for radio electronics look very promising. Iron titanates possess the properties of magnetic semiconductors and in recent years they have been attracting the attention of researchers as a base for radiation-resistance magneto-electronic and spintronic devices [1 – 3].

There are various known methods of synthesizing pseudobrookite type compounds [4 – 7], including with the use of

mineral raw materials. Given a flexible production routines, making it possible to adapt technological processes to concrete raw materials taking account of their individual characteristics, the latter have obvious technical-ecological advantages. The main problems in such cases are due to the resolution of questions concerning the reproducibility and stability of the operating characteristics of the final product.

Ilmenite – leucoxene concentrate obtained by electromagnetic extraction of the ore component from placers at the Pizhenskoe titanium deposits (Republic of Komi) was used as the initial material. Separation was performed manually using an MRM-1 (TU 41-04.956–82) mineralogical magnet. X-ray fluorescence and x-ray diffraction analyses of the ilmenite-leucoxene concentrate showed the presence of rutile (32%<sup>3</sup>), anatase (3%), quartz (30%), and ilmenite (35%). The crystalline structure of the latter is strongly distorted; this is manifested in considerable broadening and shift of the diffraction peaks. The authors of [8] attribute this state of ilmenite to a transformation of its structure during leucoxenization.

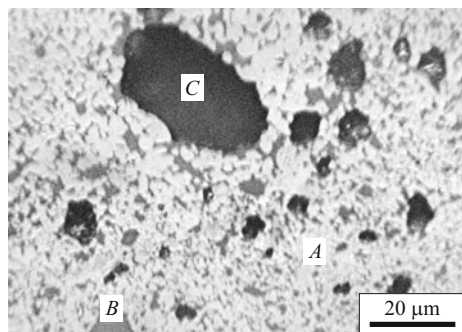
Ilmenite-leucoxene concentrate, ground and homogenized beforehand, was mixed with modifying additives: MgO — 6.0 wt.% and  $\text{Mg}_3(\text{BO}_3)_2$  — 0.5 wt.%. Cold-pressed briquettes of modified ilmenite – leucoxene concentrate (MILC) were heat-treated in a vacuum electric furnace in a continuous heating regime to 1200°C at rate 300 K/h and soaking time 1 h at the maximum temperature.

The physical-mechanical tests performed on the samples obtained included hydrostatic measurement of the apparent

<sup>1</sup> Institute of Chemistry at the Komi Science Center of the Ural Branch of the Russian Academy of Sciences, Syktyvkar, Russia.

<sup>2</sup> E-mail: grass-ve@chemi.komisc.ru.

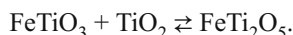
<sup>3</sup> Here and below — the molar content unless otherwise stated.



**Fig. 1.** Photomicrograph (LOMO) of ferropseudobrookite material obtained by vacuum-heat-treatment of MILC: *A* (light grains)] ferropseudobrookite phase; *B* (grey region)] silicate phase; *C* (black region)] pores.

density and porosity of the materials as well as a determination of the strength under three-point bending. The chemical and phase compositions of the samples were checked by x-ray fluorescence spectroscopy (Horiba MESA-500W) and x-ray diffractometry (Shimadzu XRD-6000). The full-profile analysis of the x-ray diffraction patterns was performed with the program POWDER CELL v. 2.4 [9] and the ICSD data base [10]. The microstructure of the materials was investigated by optical microscopy (LOMO Polam R-312), scanning electron microscopy, and energy-dispersive microprobe analysis (Jeol JSM-6400). The electrophysical properties of the samples were studied by impedance-spectroscopy using a measurement facility based on am MT4090 ac current bridge. Thermo-emf measurements were performed by the potentiometric method, using a B7-34A voltmeter, in the temperature interval from 20 to 200°C.

A series of chemical and phase transformation occur during heat-treatment of MILC. One of the main processes is high-temperature interaction of ilmenite  $\text{FeTiO}_3$  and rutile  $\text{TiO}_2$ , which for an equimolar ratio of the reagents results in the formation of ferropseudobrookite  $\text{FeTi}_2\text{O}_5$  [11–14]:

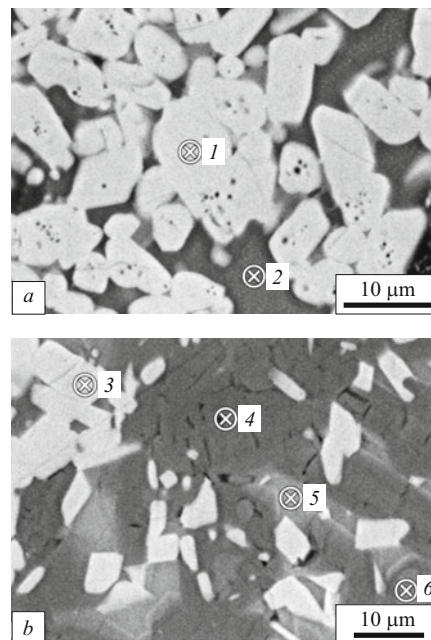


Provided that stoichiometry is maintained, this reaction is reversible but the presence of oxide impurities, specifically  $\text{MgO}$ , in the system promotes stabilization of the crystal structure of ferropseudobrookite [11]. This effect is often seen in geo- and cosmochemical processes [5, 15].

The behavior of the silicate component is important for heat-treatment of MILC. At high temperatures quartz melts, forming on cooling a glass phase which promotes sintering of the material.

Thus, during heat-treatment of MILC synthesis of the composite material consisting of semiconducting (ferropseudobrookite) and dielectric (silicate) phases occurs as a result of the processes named above.

Optical microphotography and electron-microscopic images of a polished section of the material studied are presented in Figs. 1 and 2. The main elements of the microstruc-



**Fig. 2.** Electron-microscopic images (Jeol) of the microstructure of material obtained by vacuum-heat-treatment of MILC. The elemental composition of the phases according to the data from energy-dispersive microprobe spectroscopy (at.%): 1) 21.0 Ti, 8.8 Fe, 3.6 Mg, 0.7 Al, 0.4 Mn, 65.5  $\text{O}^{\text{calc}}$  (ferropseudobrookite); 2) 20.6 Si, 2.3 Al, 1.8 Ti, 1.7 Fe, 1.7 K, 71.8  $\text{O}^{\text{calc}}$  (silicate phase); 3) 21.4 Ti, 8.6 Fe, 4.1 Mg, 0.8 Al, 0.3 Mn, 64.7  $\text{O}^{\text{calc}}$  (ferropseudobrookite); 4) 16.3 Si, 14.9 Mg, 2.6 Fe, 0.6 Mn, 0.5 Al, 0.4 Ti, 64.7  $\text{O}^{\text{calc}}$  (silicate phase); 5) 10.8 Si, 5.8 Al, 4.1 Fe, 1.8 Mg, 1.2 Mn, 0.9 Ca, 0.7 K, 74.6  $\text{O}^{\text{calc}}$  (silicate phase); 6) 20.4 Mg, 12.3 Si, 5.2 Fe, 0.8 Mn, 0.6 Al, 0.1 Ti, 60.6  $\text{O}^{\text{calc}}$  (silicate phase).

ture are ferropseudobrookite grains reaching 10  $\mu\text{m}$  in size, a silicate phase uniformly filling the intergrain space, and pores ranging in size from several to hundreds of microns. The open porosity of the material measured by the hydrostatic method does not exceed 10% but the level of the closed porosity is much higher. The apparent density of the material is 3.33  $\text{g}/\text{cm}^3$ .

The size of the ferropseudobrookite grains (point 1 and 3 in Fig. 2) varies from 1 to 100  $\mu\text{m}$ , and the chemical composition of expressed by the statistical-average formula  $\text{Fe}_{0.75}\text{Ti}_{1.8}\text{Mg}_{0.35}\text{Al}_{0.05}\text{Mn}_{0.05}\text{O}_5$ . The magnesium, aluminum, and manganese impurities do not contribute substantial distortions in the geometry of the crystal lattice of ferropseudobrookite, which possesses orthorhombic symmetry, belongs to the space group  $Cmcm$ , and possesses the following unit-cell parameters (nm):  $a = 0.37367$ ,  $b = 0.97676$ , and  $c = 1.00157$ .

According to x-ray fluorescence and x-ray diffraction analyses the amount of ferrotitanate in the products of heat-treatment of MILC is about 70%. The remaining volume is filled with a silicate phase (points 2, 4–6 in Fig. 2). The amount of protoenstatite  $\text{MgSiO}_3$  and quartz  $\alpha\text{-SiO}_2$

TABLE 1.

Element	Ilmenite – leucoxene concentrate		Product of vacuum-heat treatment of MILC	
	content, wt.%	content, at.%	content, wt.%	content, at.%
Ti	52.43	49.1	46.91	41.7
Fe	28.63	22.7	29.44	22.6
Si	12.38	19.6	11.68	17.9
Al	3.43	5.8	2.15	3.4
Mn	2.01	1.8	1.78	1.3
K	0.57	0.7	0.52	0.6
Zn	0.19	0.1	–	–
Ca	–	–	0.16	0.2
Sr	0.22	0.1	0.11	< 0.1
Nb	0.10	< 0.1	0.08	< 0.1
Zr	0.04	< 0.1	0.05	< 0.1
Y	–	–	0.04	< 0.1
Mg	–	–	7.08	12.3

does not exceed 6% and 4%, respectively, and the most of the silicate phase is in a cryptocrystalline or amorphous state.

The normalized atomic composition (neglecting the light elements) of the initial ilmenite-leucoxene concentrate and its thermal conversion products, as represented in the data obtained by quantitative x-ray fluorescence analysis, are presented in Table 1. The x-ray diffraction pattern of the material obtained as a result of vacuum heat-treatment of MILC is presented in Fig. 3.

Despite its high porosity the mechanical characteristics of the material obtained are good. Specifically, the limit of its bending strength is 100 – 130 MPa.

An investigation of the electrophysical properties established that the material is an *n*-type semiconductor. The Seebeck constant at 100 – 200°C is negative and equals 0.41 mV/K in absolute magnitude. The conductivity of the material depends weakly on the frequency of the current and strongly on the temperature. The activation energy is 0.206 – 0.216 eV at temperatures below 250°C and 0.429 – 0.435 eV at higher temperatures, which is in quite good agreement with the known properties of iron titanates [3]. The temperature dependence of the conductivity presented in Arrhenius coordinates is shown in Fig. 4a.

In the course of the electrophysical tests substantial changes in the characteristics of the material were observed with each successive measurement cycle — its conductivity and electric capacitance decrease gradually (Fig. 4b). The degradation of the conductivity is probably due to a decrease in the number of oxygen vacancies and, in consequence, a decrease of the mobility of oxygen ions. It was established that a thermal load on the material under the conditions of the air atmosphere causes its surface layer to oxidize, which is seen visually as the appearance of faint brown tint, indicating the presence of ferri ions.

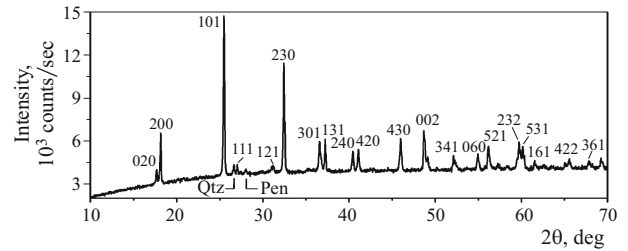


Fig. 3. X-ray diffraction pattern of ferropseudobrookite material obtained as a result of vacuum-heat-treatment of MILC: Pen) protoenstatite; Qtz) quartz.

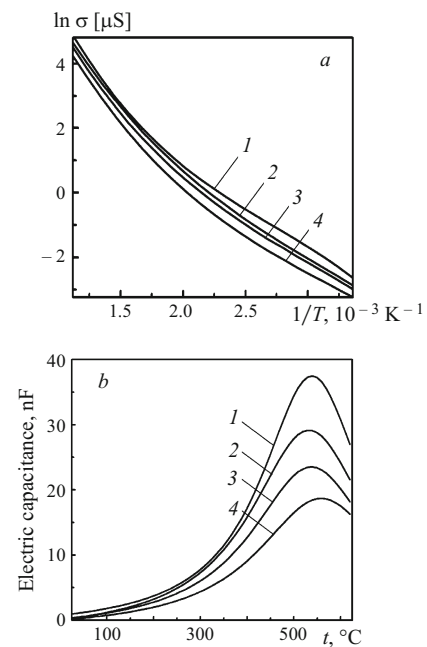


Fig. 4. Logarithm of the conductivity of samples versus the reciprocal of the temperature for current frequency 120 z (a) and electric capacitance of the samples versus the temperature at current frequency 10 kHz (b): 1) first cycle of the measurements (performed on the first day after synthesis); 2) second cycle of the measurements (performed three days after synthesis); 3) third cycle of the measurements (performed six days after synthesis); 4) fourth cycle of the measurements (performed 16 days after synthesis). The measurements were performed on 20 mm in diameter and 4 mm thick cylindrical samples.

The technological principles of the thermochemical conversion of the mineral titanium raw material are extremely simple, easily adaptable to production possibilities of mining-enrichment and reprocessing enterprises, and can serve as a basis for organizing small-tonnage production of ferro-titanate materials.

Porous silicate-ferropseudobrookite composite was synthesized as a result of the vacuum heat-treatment of the ilmenite – leucoxene concentrate modified by additions of magnesium oxide. Because of its combination of mechanical and electrophysical properties the material has wide prospec-

tive applications in electric technology. The fact that high heat loads under oxidative conditions degrade the operating properties of the composite material must be taken into account.

*We wish to thank our colleagues S. T. Neverov and V. N. Filippov at the Institute of Geology at the Komi Science Center of the Ural Branch of the Russian Academy of Sciences for assisting in the analytical work.*

## REFERENCES

1. M. A. Madare and S. V. Salvi, "Magnetic behavior of 'lithiated'  $\text{Fe}_2\text{TiO}_5$ ," *Turk. J. Phys.*, **29**(1), 25 – 31 (2005).
2. R. K. Pandey, H. Stern, W. J. Geerts, P. Padmini, P. Kale, J. Dou, and R. Schad, "Room temperature magnetic-semiconductors in modified iron titanates: their properties and potential microelectronic devices," *Adv. Sci. Techn.*, **54**, 216 – 222 (2008).
3. R. K. Pandey, P. Padmini, R. Schad, et al., "Novel magnetic-semiconductors in modified iron titanates for radhard electronics," *J. Electroceram.*, **22**(1 – 3), 334 – 341 (2009).
4. K. Hirota and R. C. Bradt, "Sintering and synthesis of the pseudobrookite oxide ( $\text{Fe}_2\text{TiO}_5$ ) by the solid state reaction," *Anal. Sci.*, **7** (suppl.), 1275 – 1278 (1991).
5. A. Ya. Medvedev, "Synthetic armalcolite and pseudobrookite," *Mineral. Mag.*, **60**(4), 347 – 353 (1996).
6. F. C. Gennari, J. J. Andrade Gamboa, and D. M. Pasquevich, "Formation of pseudobrookite through gaseous chlorides and by solid-state reaction," *J. Mater. Sci.*, **33**(6), 1563 – 1569 (1998).
7. H. Kozuka and M. Kajimura, "Sol – Gel Preparation and photo-electrochemical properties of  $\text{Fe}_2\text{TiO}_5$  thin films," *J. Sol-Gel Sci. Techn.*, **22**(1 – 2), 125 – 132 (2001).
8. V. D. Ignat'ev and I. N. Burtsev, *Timan Leucosene: Mineralogy and Problems of Technology* [in Russian], Nauka, St. Petersburg (1997).
9. W. Kraus and G. Nolze, "POWDER CELL — a program for the representation and manipulation of crystal structures and calculation of the resulting x-ray powder patterns," *J. Appl. Cryst.*, **29**(3), 301 – 303 (1996).
10. A. Belsky, M. Hellenbrandt, V. L. Karen, and P. Luksch, "New developments in the inorganic crystal structure database (ICSD): Accessibility in support of materials research and design," *Acta Cryst. B*, **58**(3), 364 – 369 (2002).
11. A. Navrotsky, "Thermodynamics of formation of some compounds with the pseudobrookite structure and of the  $\text{Fe}_2\text{TiO}_5$  –  $\text{Ti}_3\text{O}_5$  solid solution series," *Amer. Mineral.*, **60**(3 – 4), 249 – 256 (1975).
12. R. G. Teller, M. R. Antonio, A. E. Grau, et al. "The chemistry of the thermal decomposition of pseudobrookite ferrous titanium oxides," *J. Solid State Chem.*, **88**(2), 351 – 367 (1990).
13. G. Eriksson, A. D. Pelton, E. Woermann, and A. Ender, "Measurement and thermodynamic evaluation of phase equilibria in the Fe – Ti – O system," *Berich. Bunsen. Gesell.*, **100**, 1839 – 1849 (1996).
14. J. Pesl and R. H. Eriç, "High-temperature phase relations and thermodynamics in the iron – titanium – oxygen system," *Metall. Mater. Trans. B*, **30**(8), 695 – 705 (1999).
15. C. Thacker, Y. Liang, Q. Peng, and P. Hess, "The stability and major element partitioning of ilmenite and armalcolite during lunar cumulate mantle overturn," *Geochim. Cosmochim. Acta*, **73**, No. 3, 820 – 836 (2009).